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Incorporation of Nitrogen in Alkaline Earth Aluminate Glasses

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The formation and structure of silicon-free calcium aluminate and magnesium calcium aluminate oxynitride glasses have been discussed on the basis of chemical analysis of N incorporated in glasses, melting behavior of the glass, X-ray diffraction and ^{27}Al NMR spectroscopy. The aluminate glasses are characterized by the networks which are constituted of AlO_4 structural units. It has been shown that N atoms are hardly incorporated into the networks of the aluminate glasses, that is, $Al(O, N)_4$ units are not formed, but N atoms added to the batch as AlN form clusters or particles of AlN, which consists of AlN_4 structural units.

KEY WORDS: Oxynitride glass/ Structure/ NMR/ IR

1. INTRODUCTION

In recent years, many efforts have been made to understand the structure of silicate oxynitride glasses containing Al_2O_3. The incorporated nitrogen atoms do form bondings with Si atoms, but whether Al-N bonds exist or not remains controversial. Aujla[1] reported the formation of Al-N bonds in Y-Al-Si-O-N glasses on the basis of ^{29}Si NMR spectra. Hater et al.[2] also reported that ^{29}Si NMR and ^{27}Al NMR spectra suggest the presence of Al-N bonds in Mg-Al-Si-O-N glasses. Although these authors assumed the presence of Al-N bonds in aluminosilicate oxynitride glasses, no clear evidence for that has not been shown. Contrarily, Sato et al.,[3] who measured ^{27}Al NMR spectra of Al-Si-O-N glasses, did not observe any chemical shift of ^{27}Al NMR spectra from that of Al_2O_3 and suggested that the concentration of Al-N bonds might be small, if any. In previous work,[4] we also found that N does not make bonds with Al in yittrium aluminosilicate glasses. This may indicate that most of N are bonded to Si in silica rich oxynitride glasses.

It is therefore interesting to discuss the structure of silica-free or silica-poor aluminate oxynitride glasses. Dovadowx et al.[5] determined the glass-formation region of Ca-Al-O-N glasses, finding that it becomes larger when nitrogen is incorporated into the CaO-Al_2O_3 system. Although Durham and Risbud[6] studied on the preparation and properties of Ba-Mg-Al-O-N glasses and low silica content Ca-Al-O-N glasses, they did not discuss the effect of incorporation of N on the structure of glass.

In present work, we will describe the results of study on the incorporation and state of nitrogen in silica-free and low-silica aluminate glasses in the CaO-Al_2O_3 and MgO-CaO-Al_2O_3

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systems. The structure of glasses prepared has been examined by X-ray diffraction and ^{27}Al MAS NMR spectra, and the incorporation of nitrogen in glasses has been discussed.

2. EXPERIMENTAL

2.1 Preparation of glasses

The compositions $61CaO\cdot(39-x)Al_2O_3\cdot 2xAlN$ (x=0, 1, 2, 3), $15MgO\cdot 61CaO\cdot(39-x)Al_2O_3\cdot 2xAlN$ (x=0, 3, 5, 8) and $15MgO\cdot 61CaO\cdot 39Al_2O_3\cdot xSi_3N_4$ (x=2.5, 5) in molar ratio were selected for the present study. The addition of MgO to compositions of the binary $CaO\text{-}Al_2O_3$ system was made from expectation that the glass formation would be easier for the ternary compositions. In all compositions, the CaO/MgO ratio was kept constant at 61/39. The compositions melted are listed in Table 1.

Table 1. Compositions, nitrogen content, melting behavior and formation of the glasses prepared in this study.

Glass	Oxide Composition /mol%			N content /wt%		Melting behavior and glass formation
	MgO	CaO	Al_2O_3	Calc.	Analysis	
$61CaO\cdot(39-x)Al_2O_3\cdot 2xAlN$						
No. 1 x=0	—	61	39	—	—	amorphous
No. 2 x=1	—	61	39	—	—	amorphous
No. 3 x=2	—	61	39	—	—	amorphous
No. 4 x=3	—	61	39	—	—	not melted
No. 5 x=4	—	61	39	—	—	not melted
$15MgO\cdot 61CaO\cdot(39-x)Al_2O_3\cdot 2xAlN$						
No. 6 6=0	15	61	39	0	0	amorphous
No. 7 x=3	15	61	39	1.09	—	amorphous
No. 8 x=5	15	61	39	1.81	1.01	amorphous
No. 9 x=8	15	61	39	2.9	1.8	amorphous+crystal
No. 10 x=10	15	61	39	—	—	not melted
$15MgO\cdot 61CaO\cdot(39-x)Al_2O_3\cdot xSi_3N_4$						
No. 11 x=2.5	15	61	36.5 15(SiO_2)	2.2	1.7	amorphous
No. 12 x=5.0	15	61	34 30(SiO_2)	—	—	bloating
No. 13 x=7.5	15	61	31.5 45(SiO_2)	—	—	not melted

The base oxide glasses were prepared by melting batches consisting of reagent grade MgO, $CaCO_3$ and Al_2O_3 chemicals in Pt-Rh crucibles at 1,500°C for 30 minutes and quenching the melt in water. The batch size was selected so that more than 10 g glass could be obtained. The obtained oxide glasses were pulverized. The mixture of the base oxide glass powder and AlN or Si_3N_4 were melted in an Ir crucible at 1,500°C for 30 min in a flow of nitrogen. The melts were taken out of the furnace and cooled down by placing the crucible in water. An Ir crucible was used for melting glass, because a BN crucible was not suitable for melting the present batches due to the dissolution of an appreciable amount of boron into the melt.

2.1 Observation of glass formation

Glass formation was confirmed by the appearance of the cooled melt. X-ray diffraction

using CuKα radiation was used to detect the precipitation of crystals in glasses.

2.2 Chemical analysis of nitrogen in the cooled melts

The nitrogen content of a glass was determined by the quantitative chemical analysis based on the Kjeldahl method. The details of the analytical procedure have been described elsewhere.[7)]

2.3 Measurement of ^{27}Al MAS NMR

The ^{27}Al NMR spectra of glasses were measured by a Nippon Denshi model JEOL GSX-400 high resolution solid state FT-MAS NMR spectrometer. The powder sample was put into a sample holder, which was spun at 5.6 kHz. The spectra were measured in a magnetic field of 9.4 T. The ^{27}Al NMR spectrum of $Al_2(SO_4)_3 \cdot nH_2O$ (n=12–14) was used as reference.

3. RESULTS

3.1 Incorporation of nitrogen in glass

The nitrogen contents of the glass determined by the chemical analysis are shown in Table 1. Fig. 1 shows the N content of the glass versus the N content of the batch for the compositions $15MgO \cdot 61CaO \cdot (39\text{-}x)Al_2O_3 \cdot 2xAlN$ and $15MgO \cdot 61CaO \cdot (39\text{-}x)Al_2O_3 \cdot xSi_3N_4$. It is seen that

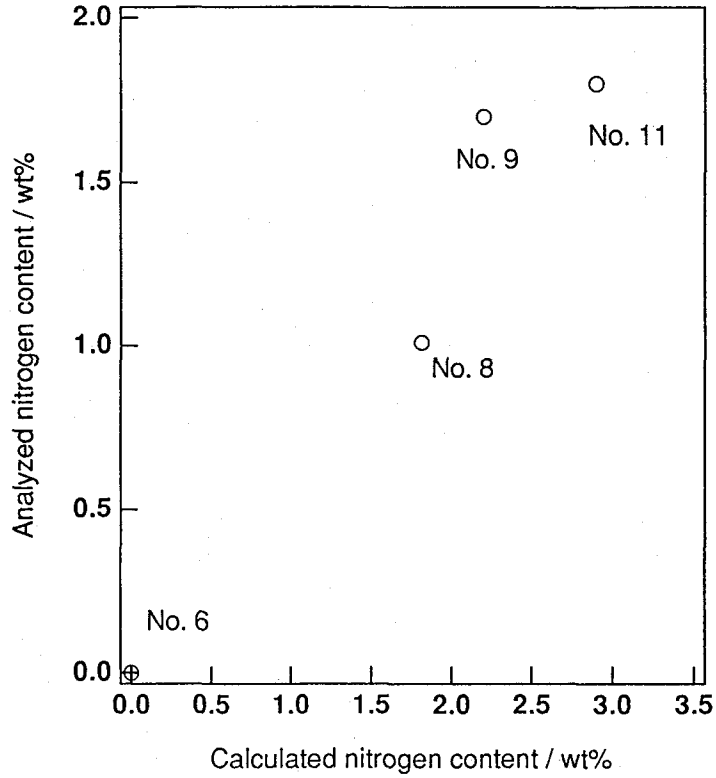


Fig. 1. The analyzed nitrogen content of glasses as a function of the nitrogen content calculated from the batch for the compositions of $15MgO \cdot 61CaO \cdot (39\text{-}x)Al_2O_3 \cdot 2xAlN$ and $15MgO \cdot 61CaO \cdot (39\text{-}x)Al_2O_3 \cdot xSi_3N_4$.

50–60% of nitrogen in the batch is retained in silicon-free alkaline earth aluminate glasses and about 70% N is retained in the glass made from the batch containing Si_3N_4.

3.2 Glass formation and apperance of the products

Observation on glass formation is described in Table 1. Fig. 2 shows the X-ray diffraction patterns of cooled melts, No. 8 and No. 9.

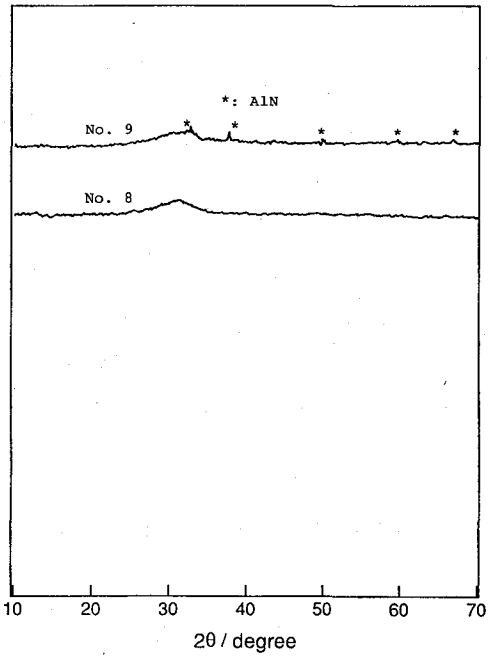


Fig. 2. X-ray diffraction patterns of the quenched melts.

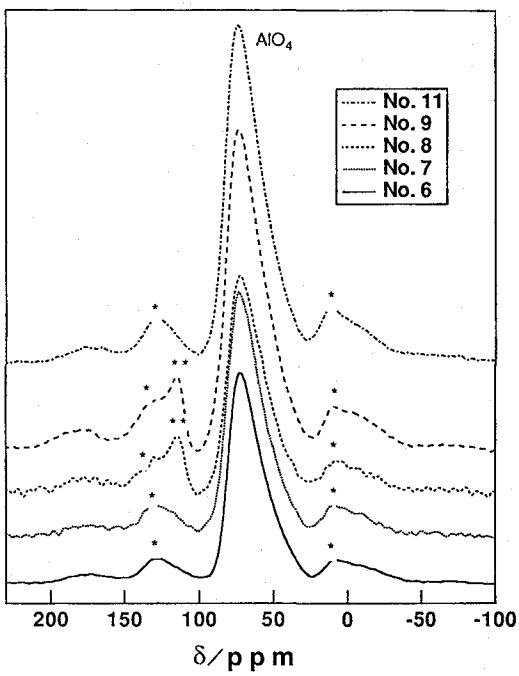
It was found that cooled melts No. 1, 2, 3, 6, 7, 8, and 11 did not have any diffraction peaks, as represented by No. 8 melt in Fig. 2. It is seen that for No. 8 the X-ray diffraction pattern consists of a broad scattering band peaking around 23–25 degrees in 2θ characteristics of the oxide glass. On the other hand, cooled melt No. 9 of the composition $15MgO{\cdot}61CaO{\cdot}31Al_2O_3{\cdot}16AlN$ shows very small peaks due to crystalline AlN which overlap with a broad band for glass (see Fig. 2). This indicates that AlN is hardly dissolved in silicon-free aluminate glasses, and nitrogen is easily precipitated as AlN without entering into the glass network.

An intensive bloating was observed in melt No. 12 to which nitrogen was added as Si_3N_4 to an alkaline earth aluminate composition. This also indicates that Si_3N_4 is not easily dissolved in the aluminate melt, but is decomposed, evolving nitrogen gas.

3.3 ^{27}Al MAS NMR spectra

^{27}Al MAS NMR spectra of glasses are shown in Fig. 3. Two meaningful bands are observed at about 70 ppm and 115 ppm. The bands found around 10 ppm and 130 ppm are the spinning side bands. The chemical shifts around 70 ppm and 115 ppm are listed in Table 2.

The 70 ppm peak is attributed to AlO_4 tetrahedral groups. This assignment is based on our previous work,[4] where the ^{27}Al MAS NMR spectra of feldspar, mullite, sillimanite, kyanite and



* spinning side band, ** AlN_4

Fig. 3. ^{27}Al MAS NMR spectra of glasses of the compositions, 15MgO·61CaO·(39-x)Al_2O_3·2xAlN and 15MgO·61CaO·(39-x)Al_2O_3·xSi_3N_4.

andalusite minerals with a well known structure for relating the spectra to the coordination state of aluminum. Similarly, the 110 ppm peak is attributed to AlN compounds. No other peak can be found between these two bands for the AlO_4 group in glass and AlN compound.

Table 2. Peak positions of ^{27}Al MAS NMR spectra of the glasses.

Glass	Oxide Composition/mol%				Analyzed N content/wt%	70 ppm band*	115 ppm band**
	MgO	CaO	Al_2O_3				
61CaO·(39-x)Al_2O_3·2xAlN							
No. 1 x=0	—	61	39		—	73.12	—
No. 2 x=1	—	61	39		—	72.78	—
No. 3 x=2	—	61	39		—	72.65	—
15MgO·61CaO·(39-x)Al_2O_3·2xAlN							
No. 6 x=0	15	61	39		0	73.59	—
No. 7 x=3	15	61	39		—	74.06	—
No. 8 x=5	15	61	39		1.01	73.59	116.25
No. 9 x=8	15	61	39		1.8	74.06	115.78
15MgO·61CaO·(39-x)Al_2O_3·xSi_3N_4							
No. 11 x=2.5	15	61	36.5	7.5(SiO_2)	1.7	72.65	—
No. 12 x=5.0	15	61	34	15 (SiO_2)	—	—	—

* AlO_4, ** AlN_4.

In Table 2, it is seen that the chemical shifts for the 70 ppm bands remain almost the same for glasses with different nitrogen contents.

4. DISCUSSION

4.1 Formation of aluminate oxynitride glasses

The present experimental results on the incorporation of nitrogen in alkaline earth aluminate glasses are summarized as follows:

(1) The quantity of nitrogen which can be incorporated into the alkaline earth aluminate glasses without causing crystallization of glass is small compared with alkaline earth silicate glasses. The quantity of nitrogen incorporated into $61CaO{\cdot}39Al_2O_3$ glass is 2.2wt% at the most, while 5.5wt% N can be incorporated in $36CaO{\cdot}24Al_2O_3{\cdot}40SiO_2$ glass.[8]

(2) Crystalline AlN is precipitated as detected by X-ray diffraction when only 1wt% of nitrogen is added to the composition $15MgO{\cdot}61CaO{\cdot}(39\text{-}x)Al_2O_3{\cdot}2xAlN$.

(3) Even when X-ray diffraction does not give any crystalline AlN peaks but does show a halo pattern, the ^{27}Al MAS NMR spectra indicate that AlN compounds are present (Glasses No. 8 and 9).

(4) Heavy bloating occurs when Si_3N_4 is added as N source to aluminate glasses of the composition $15MgO{\cdot}61CaO{\cdot}34Al_2O_3{\cdot}5Si_3N_4$. This may be caused by the evolution of N_2 gas as a result of the reaction of Si_3N_4 with aluminum oxide component in the melt.

These indicate that generally, incorporation of nitrogen in aluminate glasses is not easy. In other words, a partial substitution of nitrogens for oxygens in AlO_4 structure units constituting the glass network is diffiult due to the instability of, for example, AlO_3N units.

4.2 The state of nitrogen in aluminate glasses

It has been shown in this study that although nitrogens are hardly incorporated into aluminate glasses, a small amount of nitrogen is present in the aluminate glasses according to the chemical analysis. ^{27}Al NMR spectra in Fig. 3 indicate that nitrogen may essentially be present as AlN compounds. It is suspected, however, that there may be some other forms of nitrogen in glasses. This point will be discussed below on the basis of the results of ^{27}Al NMR spectra of glasses.

It has been confirmed that the network of calcium aluminate and other alkaline earth aluminate glasses consists of AlO_4 structural units connected with each other three-dimensionally.[9,10] Accordingly, if N atoms replace oxygens in the structure of nitrided aluminate glasses, $Al(O, N)_4$ structural units would be formed. The formation of such units might be possible from the fact that in β'-sialon crystals the $AlON_3$ structural units are stable.[11] It should be noted that this unit has three nitrogens and one oxygen. It is also reported[12] that AlO_2N_2 and AlO_3N structural units are formed in some oxynitride crystals, although these units are not extended through the crystal. These would indicate that AlO_2N_2 and AlO_3N units might not be stable.

We will examine the results on ^{27}Al MAS NMR spectra to see whether $Al(O, N)_4$ units are formed in the present glasses. The chemical shift of ^{27}Al MAS NMR peak for the AlO_4 is about 70 ppm and that for the AlN_4 unit is about 115 ppm. If a small amount of N would be present as AlO_3N, AlO_2N_2 or $AlON_3$ structural units, there should appear another peak between 70 ppm and 115 ppm, or the 70 ppm peak should have a low-field shift. Assuming that the unit is AlO_3N

and the nitrogen content of glass is 1–2 wt%, we can expect 1–2 ppm shift. As seen from the ^{27}Al MAS NMR data of glass No. 6 (0 wt%N), No. 7 (1.0wt%N) and No. 8 (1.8 wt%N) in Table 2, the 70 ppm peak does not show a systematic shift to low fields with an increase in nitrogen content. These show that there are no $Al(O, N)_4$ units in the present glasses, and N is present solely as AlN_4 groups which are assumed to be present in the form of very fine particles. In Fig. 3 and Table 1, glass No. 11 for which Si_3N_4 was employed as nitrogen source does not have AlN peak. It is assumed that most of nitrogen has gone during melting as shown by heavy bubbling, and a small amount of nitrogens, if any, form bonds with Si atoms.

In Y-Al-Si-O-N glass, it was shown that N does not form bonds with Al but forms bonds with Si.[4] The present results together with the information in previous work[4] can be summarized as follows : N forms bonds with Si preferentially in glasses containing both Si and Al. No bonding is possible between Al and N in glass network. This is also the case for aluminate glasses in which only Al atoms are present as network-forming cation.

5. CONCLUSION

Incorporation and structural state of nitrogen in alkaline earth aluminate glasses were studied by observation of melting behavior, X-ray diffraction patterns and ^{27}Al MAS NMR spectra of glasses.

(1) Chemical analysis of glass shows that alkaline earth aluminate glasses containing a small amount of nitrogen can be made, but the amount of N entering the glass networks is very small compared with silicate glasses.

(2) In aluminate glasses nitrogen atoms are present as very fine particles or clusters of AlN compound consisting of AlN_4 units.

(3) It is assumed from NMR spectra that N is not present as $Al(N, O)_4$ units in alkaline earth aluminate glasses. This again indicates that N does not enter the network structure of the glasses.

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